

Reactions of nitriles in ices relevant to Titan, comets, and the interstellar medium: formation of cyanate ion, ketenimines, and isonitriles

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Abstract

Motivated by detections of nitriles in Titan's atmosphere, cometary comae, and the interstellar medium, we report laboratory investigations of the low-temperature chemistry of acetonitrile, propionitrile, acrylonitrile, cyanoacetylene, and cyanogen (CH₃CN, CH₃CH₂CN, CH₂CHCN, HCCCN, and NCCN, respectively). A few experiments were also done on isobutyronitrile and trimethylacetonitrile ((CH₃)₂CHCN and (CH₃)₃CCN, respectively). Trends were sought, and found, in the photo- and radiation chemical products of these molecules at 12–25 K. In the absence of water, all of these molecules isomerized to isonitriles, and CH₃CN, CH₃CH₂CN, and (CH₃)₂CHCN also formed ketenimines. In the presence of H₂O, no isonitriles were detected but rather the cyanate ion (OCN[−]) was seen in all cases. Although isonitriles, ketenimines, and OCN[−] were the main focus of our work, we also describe cases of hydrogen loss, to make smaller nitriles, and hydrogen addition (reduction), to make larger nitriles. HCN formation also was seen in most experiments. The results are presented in terms of nitrile ice chemistry on Titan, in cometary ice, and in the interstellar medium. Possible connections to prebiotic chemistry are briefly discussed.

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1. Introduction

Nitriles and nitrile chemistry are found in a variety of astrochemical environments, have been used to understand many observations, and have been invoked in diverse areas of astronomy and planetary science. As examples, HCN and the CN radical have long been known to be in cometary coma (e.g., Woodney et al., 2002; Huggins, 1882; Magee-Sauer et al., 1999), molecules with cyano (C≡N) groups have been used to understand the color of several D-class asteroids (Cruikshank et al., 1991), the cyanopolyynes series HC_nCN ($n = 0, 2, 4, \dots, 10$) is found in the interstellar medium (Bell et al., 1998), chemical models for circumstellar envelopes involve CN reactions (Mebel and Kaiser,

2002), and a spectral band of OCN[−] is seen in an ISO spectrum of an embedded protostar (Hudson et al., 2001; van Broekhuizen et al., 2004; and references therein). Astrobiologists have a well-established interest in nitriles going back at least 40 years (Oró, 1961). In a recent study, Levy et al. (2000) examined possible prebiotic formation of adenine and amino acids on Europa by analyzing NH₄CN solutions stored at −20 and −78 °C for 25 years.

Within the Solar System, nitrile chemistry is particularly relevant to Titan. This saturnian satellite has a surface temperature near 94 K, and a 1.5-bar atmosphere of ~95% N₂ and 5% CH₄, and so offers the possibility of extensive nitrile formation and reactions stimulated by cosmic radiation, UV photons, the saturnian magnetosphere and (possibly) lightning (Samuelson, 2003). Four gas-phase nitriles already have been identified in Titan's atmosphere (HCN, CH₃CN, HCCCN, and NCCN), and a fifth (NCCCCN) has been detected as a solid (Coustenis et al., 1999). Theoretical models

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of Titan chemistry suggest that nitrile formation is initiated by the gas-phase dissociation of N_2 (McKay et al., 2001; Lara et al., 1996; and references therein) and that the nitriles themselves eventually accumulate on Titan's surface.

Astrochemists have long been drawn to the challenge of exploring Titan chemistry in a terrestrial laboratory. A complete review of Titan simulations and models is far beyond the scope of this paper, but would certainly include Scattergood et al. (1975), Gupta et al. (1981), Ferris and Morimoto (1981), Khare et al. (1984), Thompson et al. (1991), Coll et al. (1995), Clarke and Ferris (1997), Fujii and Arai (1999), Coll et al. (1999), and Navarro-González et al. (2001), among many others. In a typical laboratory experiment, a mixture of Titan molecules, such as $N_2 + CH_4$, is subjected to some type of energy input, such as plasma discharge, UV photolysis, spark discharge, or particle bombardment, and the resulting chemical products analyzed. The subsequent analyses usually have involved a chromatographic method, often coupled with mass spectrometry. For example, Coll et al. (1999) have impressively identified more than forty hydrocarbons and over twenty nitrogen-containing compounds in a single Titan simulation. Fujii and Arai (1999) reported over seventy products from their Titan experiment, including twenty-four nitriles and ten amines.

Since essentially all laboratory workers and astronomical observers agree that nitriles are important for understanding Titan's chemistry, the reactions of these molecules are of interest. However, while the astrochemical literature contains reliable low-temperature spectral data for many nitriles (e.g., Dello Russo and Khanna, 1996; Bernstein et al., 1997), relatively little has been published on the solid-phase chemistry of these compounds. Perhaps one reason for this neglect among astrochemists is the reputation of these molecules for polymerizing into unwieldy solids. For example, it has been known for over a century that cyanogen (NCCN) forms a refractory material known as paracyanogen (Lind, 1928), which has been proposed as a constituent of asteroidal material (Cataldo, 1992). The major radiation product of acetonitrile (CH_3CN), another Titan molecule, is an ill-defined solid (Asycough et al., 1968), and acrylonitrile (CH_2CHCN) polymerizes with almost any source of energy, forming a poorly-soluble material.

In this paper we describe recent experiments on reactions of acetonitrile, propionitrile, isobutyronitrile, trimethylacetonitrile, acrylonitrile, cyanoacetylene, and cyanogen. Structures for each of these are given in Table 1. Results of photo- and radiation chemical experiments are presented, and products are described which might be difficult to detect in room temperature mass spectral analyses. By using low ($T < \sim 100$ K) temperatures and thin ice films for our experiments, we have avoided many of the problems in working with bulk samples. Our experiments were conducted with an eye toward Titan applications, but they also may have implications to interstellar and cometary chemistry, and astrobiology as well.

Table 1
Nitrile molecules investigated

Molecule	Structure	Observed on Titan?	Seen in cometary comae?	Known interstellar molecule?
CH_3CN acetonitrile (methyl cyanide)	$\begin{array}{c} H \\ \\ H-C-CN \\ \\ H \end{array}$	Yes	Yes	Yes
$(CH_3)CH_2CN$ propionitrile (ethyl cyanide)	$\begin{array}{c} H \\ \\ H_3C-C-CN \\ \\ H \end{array}$	No	No	Yes
$(CH_3)_2CHCN$ isobutyronitrile (isopropyl cyanide)	$\begin{array}{c} H \\ \\ H_3C-C-CN \\ \\ CH_3 \end{array}$	No	No	No
$(CH_3)_3CCN$ trimethylacetonitrile (<i>tert</i> -butyl cyanide)	$\begin{array}{c} CH_3 \\ \\ H_3C-C-CN \\ \\ CH_3 \end{array}$	No	No	No
CH_2CHCN acrylonitrile (vinyl cyanide)	$\begin{array}{ccc} H & & H \\ & \diagdown & / \\ & C=C & \\ & / & \diagdown \\ H & & CN \end{array}$	No	No	Yes
HCCCN cyanoacetylene	$HC\equiv C-CN$	Yes	Yes	Yes
C_2N_2 cyanogen	$NC-CN$	Yes	No	No

For this work we considered three different chemical environments for each nitrile molecule, namely the solid nitrile itself, solid N_2 , and frozen H_2O . We exposed each sample to either vacuum-UV light or a 0.8 MeV proton beam to explore the chemistry induced by far-UV photons and ionizing radiation. Although proton irradiations were usually more efficient in carrying out chemical change, in some cases they were not done for fear of damaging or contaminating the experimental apparatus with undesirable, refractory polymeric products. From this vantage point, the "safest" experiments were those involving N_2 matrices, and so these were done on all nitriles. All compounds were studied in H_2O -ice and, with the exception of pure cyanogen, each compound was also studied in the pure state.

2. Experimental methods

Since our experimental procedures are already in print, we present only a summary here. Additional information can be found in, for example, Moore and Hudson (2003) and references therein.

Ice samples typically were prepared by vapor-phase condensation onto a precooled (12–25 K) aluminum substrate in a high-vacuum chamber. Ice thicknesses of several micrometers were reached in about 1 h, with thicknesses being

Table 2
Properties of 0.8 MeV protons and target materials

Ice	Stopping power (MeV cm ² g ⁻¹) ^a	p ⁺ range (μm) ^a	Number eV mole- cule ⁻¹ equivalent to 1 × 10 ¹⁴ p ⁺ cm ⁻²	Target density (g cm ⁻³)
CH ₃ CN	284.8	23	1.9	0.80
H ₂ O	273.8	19	0.82	1.00
N ₂	235.3	21	1.06	1.03

^a Calculated with the SRIM software of Ziegler at <http://www.srim.org/>.

measured with a laser interference system. In some experiments, ices were made by injecting a room-temperature liquid-phase solution onto a precooled substrate. In all cases, the ices made and studied were amorphous.

Ice samples were irradiated with 0.8 MeV protons from a Van de Graaff accelerator to doses of 1–15 eV per molecule. For the use of proton radiolysis to mimic cosmic ray bombardment see Moore et al. (2001). Table 2 summarizes the radiation stopping powers and ranges used in our work, as calculated from Ziegler's SRIM program (Ziegler et al., 1985), along with ice densities. Since sample thicknesses were on the order of a few micrometers, the bombarding protons penetrated the ices and came to rest in the underlying metal substrate, not in the ices themselves. Radiation doses were monitored by following the proton fluence (number of protons cm⁻²) during experiments. Conversions to the more convenient unit of "eV molecule⁻¹" are in Table 2.

Far-UV photolyses were performed with a microwave-discharge hydrogen-flow lamp (Gerakines et al., 2004; Allamandola et al., 1988) having about 90% of its output in the 157–170 nm (7.9–7.3 eV) region, with Ly α photons (10.2 eV, 121.6 nm) for the remainder. This lamp's spectrum has been published and shows an average energy of 7.41 ± 0.23 eV per photon (Cottin et al., 2001). The lamp flux varied over a period of months, but the average value was about 2.0 × 10¹⁴ photons cm⁻² s⁻¹ with a variation of about a factor of two. A quantitative photophysical comparison of ion irradiation and UV-photolytic efficiencies would require a more detailed analysis of the photon flux, but for the chemical applications presented here the 2.0 × 10¹⁴ photons cm⁻² s⁻¹ value is sufficient. For a similar approach, see recent UV-papers of Bernstein et al. (2004), van Broekhuizen et al. (2004), and Peeters et al. (2003).

Infrared (IR) spectra of ices usually were recorded as 60-scan accumulations, typically at a resolution of 4 cm⁻¹ from 4000 to 400 cm⁻¹. A few experiments, mostly those with N₂ as a matrix, were performed with 120-scan accumulations at 1 cm⁻¹ resolution. An IR band's integrated intensity $\int \tau(\tilde{\nu}) d\tilde{\nu}$, in cm⁻¹, could be converted to a molecular column density N , in molecule cm⁻², through

$$N = \frac{\int \tau(\tilde{\nu}) d\tilde{\nu}}{A}$$

provided that the band's intrinsic strength, A in cm molecule⁻¹, was known. The band strengths, in cm molecule⁻¹,

used in this paper are 2.2 × 10⁻¹⁸ for CN stretches of nitriles and isonitriles (Section 3.1), 5.1 × 10⁻¹⁸ for HCN near 2090 cm⁻¹ (Bernstein et al., 1997), and 8.0 × 10⁻¹⁸ for CH₄ near 1300 cm⁻¹ (Kerkhof et al., 1999). Since we were unable to find a band strength for ketenimine, H₂C=C=NH, a value of 7.2 × 10⁻¹⁷ cm molecule⁻¹ (J. Keane, personal communication) was adopted, based on the isoelectronic molecule HNCO.

Chemical reagents for experiments were purchased largely from Aldrich, Matheson, and Cambridge Isotopes, and used as received. Cyanoacetylene was a gift from L. Stief (NASA/Goddard) and H. Okabe (Catholic University of America). Its purity was confirmed by a comparison of its IR spectrum with that of a reference sample (Dello Russo and Khanna, 1996), and so it was used as received.

3. Results

Experimental results will be presented in five sections. First we describe experiments on CH₃CN, followed by results on three other saturated nitriles but emphasizing CH₃CH₂CN. We next consider unsaturated nitriles (those with C=C and C≡C bonds) and cyanogen. We then turn to nitrile experiments involving H₂O-ice, and end with a brief consideration of residual materials. Although these experiments yielded many interesting results, our emphasis is on laboratory observations with potential astrochemical or astrobiological applications. We focus on reactions and reaction products that appear common to all nitriles, and that have received little coverage elsewhere. No attempt has been made to identify every possible reaction product for each compound or to assign every spectral feature. In future papers we hope to address the problems of reaction yields from nitriles and the relevant infrared band strengths.

3.1. Acetonitrile, CH₃CN

Acetonitrile (methyl cyanide, CH₃CN) is the simplest organic nitrile, and is observed in cometary comae, in Titan's atmosphere, and in interstellar space. As shown in Table 1, CH₃CN is also the simplest member of the series (CH₃)_{*m*}CH_{3-*m*}CN where *m* = 0, 1, 2, 3. Figure 1 shows IR spectra for CH₃CN deposited at 18 K and slowly warmed. Spectra from 18 to 100 K are for amorphous CH₃CN, while the changes at 105 K are due to the sample's crystallization, presumably into the orthorhombic β -phase (Torrie and Powell, 1992). Above 155 K the sample was quickly lost due to sublimation within our vacuum system. Allowing for differences in temperatures, good agreement exists between the spectra of Fig. 1 and published spectra of amorphous (d'Hendecourt and Allamandola, 1986) and crystalline (Dello Russo and Khanna, 1996) CH₃CN.

To help quantify our work, we determined the intrinsic band strength, A , of the intense C≡N stretching vibration ($\nu_2 = 2252$ cm⁻¹) of amorphous CH₃CN. The thick-

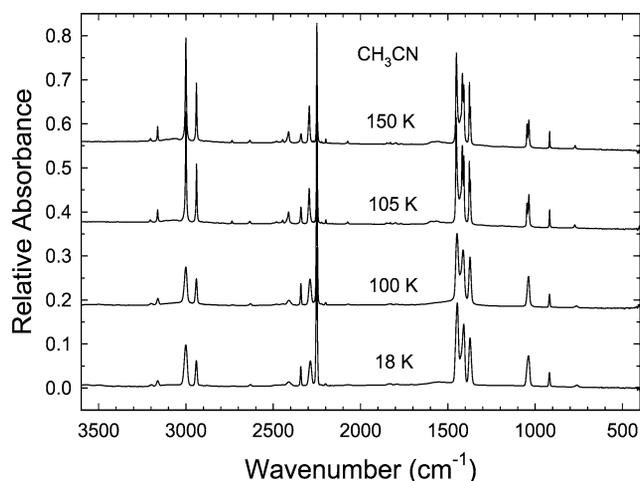


Fig. 1. IR spectra of CH_3CN deposited at 18 K and warmed. A small, sharp feature at 2340 cm^{-1} is due to CO_2 . The thickness of the sample was about $1.25\text{ }\mu\text{m}$.

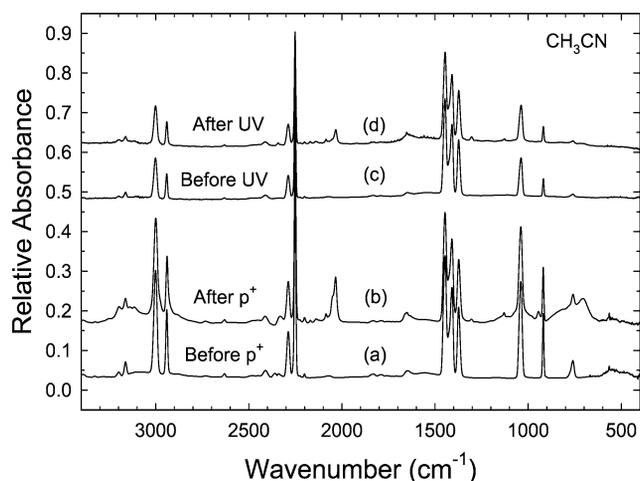


Fig. 2. IR spectra of two amorphous CH_3CN samples. The first is shown (a) before and (b) after ion irradiation to a dose of about $1\text{ eV molecule}^{-1}$, and the second is shown (c) before and (d) after a 90-min UV photolysis. Sample temperatures were $\sim 18\text{ K}$ for (a) and (b) and 12 K for (c) and (d).

ness of the sample from Fig. 1 was measured (see above) and combined with an assumed density of 0.8 g cm^{-3} to calculate a CH_3CN column density, N . (The density was taken from liquid acetonitrile since amorphous solids have close structural similarities to liquids.) The value of N was then substituted into the above equation, along with the integrated intensity of the $\text{C}\equiv\text{N}$ band, to give $A = 2.2 \times 10^{-18}\text{ cm molecule}^{-1}$, in good agreement with an earlier value of $2.3 \times 10^{-18}\text{ cm molecule}^{-1}$ (d'Hendecourt and Allamandola, 1986). As a check on our value, we warmed the amorphous CH_3CN sample until it crystallized at 105 K, measured the area of the $\text{C}\equiv\text{N}$ feature, and then applied the optical constants of Dello Russo and Khanna (1996) for crystalline CH_3CN . This gave the CH_3CN column density in our crystalline sample. Assuming that the amorphous and crystalline samples had the same column density (only approximately correct), we used the above equation a second

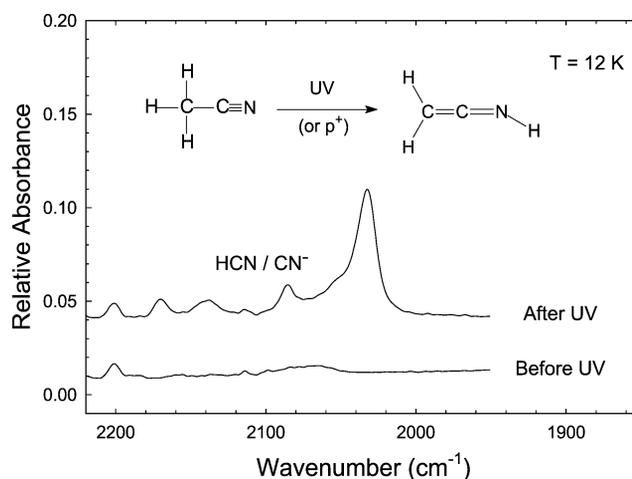


Fig. 3. IR spectra of CH_3CN before and after a 90-min UV photolysis at 12 K.

time, obtaining $A(\text{C}\equiv\text{N}) = 1.9 \times 10^{-18}\text{ cm molecule}^{-1}$, in reasonable agreement with our other value. Throughout this paper we take $A(\text{C}\equiv\text{N}) = 2.2 \times 10^{-18}\text{ cm molecule}^{-1}$ for all organic nitriles.

Figure 2 compares IR spectra of amorphous CH_3CN (a) before and (b) after 0.8 MeV proton irradiation to spectra of a separate sample (c) before and (d) after a 90-min UV photolysis. Growth of a feature near 2030 cm^{-1} is seen in both samples and, in general, the IR spectra for the two experiments indicated formation of similar products.

Figure 3 is an enlargement of the spectra from the UV experiment, showing the $2220\text{--}1950\text{ cm}^{-1}$ region. Several new bands can now be seen in the post-photolysis spectrum, the most prominent being at 2033 cm^{-1} . Correlated with the growth of this feature was a weaker band at 1129 cm^{-1} (not shown). Both bands rose together in all experiments and showed a sharp decline as the sample was subsequently warmed above $\sim 105\text{ K}$, where CH_3CN crystallized. Two experiments suggested an assignment of these features to ketenimine, $\text{H}_2\text{C}=\text{C}=\text{NH}$. First, we independently synthesized $\text{H}_2\text{C}=\text{C}=\text{NH}$ by a photochemical reaction of HN_3 and C_2H_2 at 12 K (Jacox and Milligan, 1963), and observed the 2033 cm^{-1} feature of Fig. 3 (and the 1129 cm^{-1} band, not shown). Second, we photolyzed CD_3CN at 12 K, and observed a shift of the 2033 cm^{-1} band to 1997 cm^{-1} , the known position of the ν_3 vibration of $\text{D}_2\text{C}=\text{C}=\text{ND}$ (Jacox, 1979).

Taken together, these observations imply that a rearrangement, $\text{CH}_3\text{CN} \rightarrow \text{H}_2\text{C}=\text{C}=\text{NH}$, took place. Additional experiments confirmed that our reaction was intramolecular (involving individual CH_3CN molecules). We first photolyzed a $\text{CH}_3\text{CN}:\text{CD}_3\text{CN}$ ($\sim 1:1$) mixture. As seen in Fig. 4, only two bands, at 2033 and 1997 cm^{-1} , appeared in the region of Fig. 3. (Ketenimines such as $\text{H}_2\text{C}=\text{C}=\text{ND}$ and $\text{D}_2\text{C}=\text{C}=\text{NH}$ have positions between 2033 and 1997 cm^{-1} (Jacox and Milligan, 1963).) Next, we photolyzed CH_3CN isolated in N_2 ($\text{N}_2:\text{CH}_3\text{CN} = 100:1$), and again observed growth of a band near 2033 cm^{-1} .

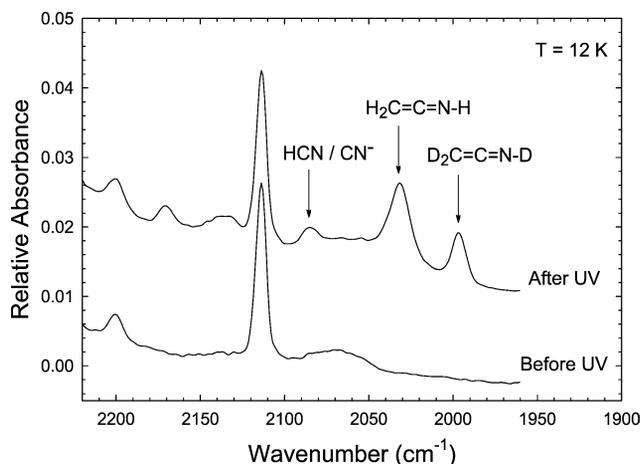


Fig. 4. IR spectra of $\text{CH}_3\text{CN} + \text{CD}_3\text{CN}$ ($\sim 1 : 1$) before and after a ~ 90 -min UV photolysis at 12 K.

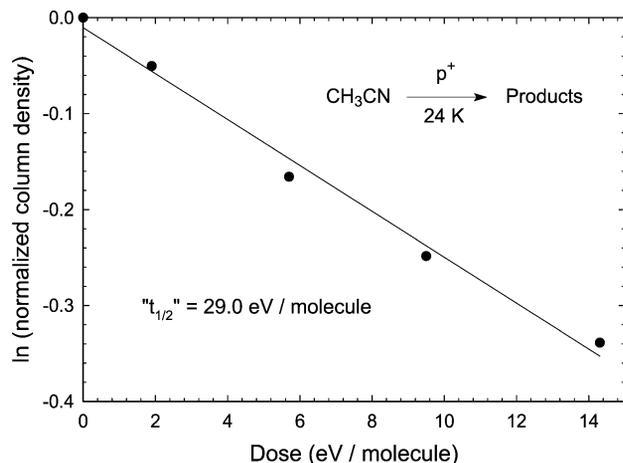


Fig. 5. Destruction of CH_3CN at 24 K by 0.8 MeV p^+ .

Proton irradiations of amorphous CH_3CN (and CD_3CN) gave essentially the same spectra, and products, as the UV photolysis experiments. An experiment in which a $\text{N}_2 + \text{CH}_3\text{CN}$ (100 : 1) mixture was proton irradiated also showed $\text{H}_2\text{C}=\text{C}=\text{NH}$ formation. The point we wish to make here is that the same reaction $\text{CH}_3\text{CN} \rightarrow \text{H}_2\text{C}=\text{C}=\text{NH}$ occurred regardless of whether CH_3CN was UV-photolyzed or proton-irradiated, and regardless of whether the CH_3CN was “neat” (pure) or diluted in N_2 . In all cases, ketenimine was synthesized from acetonitrile.

Other reaction products were suggested by the spectra of both UV-photolyzed and proton-irradiated CH_3CN . One product that was easily identified was CH_4 , seen at $\sim 1303 \text{ cm}^{-1}$ in all CH_3CN experiments (993 cm^{-1} for CD_4 made from CD_3CN). Two other products, HCN and CH_3NC , will be identified in Section 3.2.

Although the experiments in this paper focus on identifying chemical products and reactions, a few kinetic measurements were made. Figure 5 shows the radiation-induced destruction of CH_3CN at 24 K, while Fig. 6 follows the concomitant formation of four radiation products. For com-

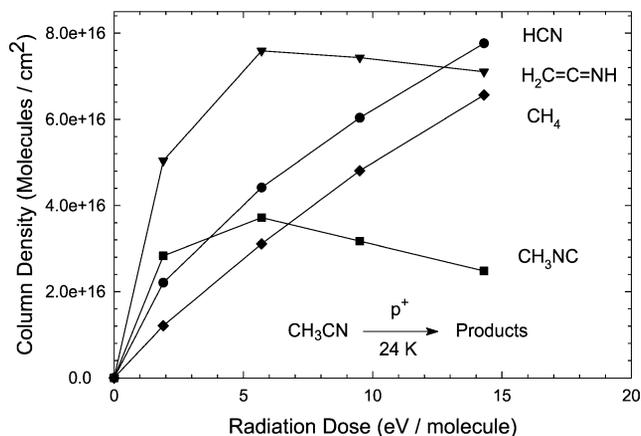


Fig. 6. Formation of products during proton irradiation of CH_3CN at 24 K.

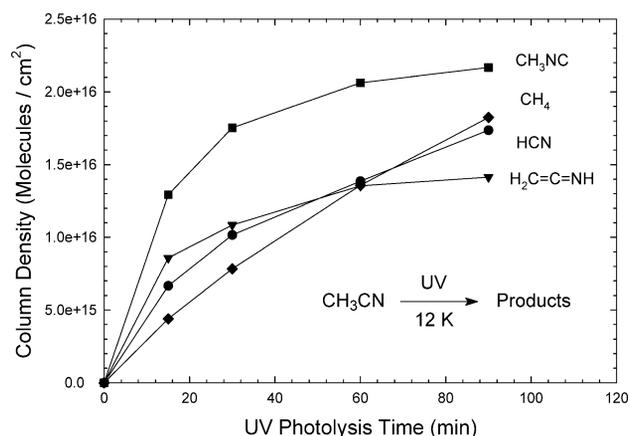


Fig. 7. Formation of products during UV photolysis of CH_3CN at 12 K. We estimate that 90 min UV $\approx 28 \text{ eV molecule}^{-1}$ for CH_3CN . See text for details.

parison, Fig. 7 shows the formation of these same products in a photolysis experiment. The temperatures in the experiments of Figs. 6 and 7 are different, but this is not thought to significantly influence the products seen. We reached this conclusion by comparing samples of CH_3CN that had been UV-photolyzed at 12 and 100 K. The destruction of CH_3CN was somewhat ($\sim \times 2$) faster at 100 than at 12 K, but the same chemical products were seen in both cases. This implied that the reactions in our experiments were driven more by the photolytic or radiolytic dose than the sample temperature. For approximate comparative purposes, note that 90-min UV photolysis $\approx 28 \text{ eV molecule}^{-1}$ for solid CH_3CN , assuming a penetration of about $0.24 \mu\text{m}$ (20% of sample’s true thickness).

3.2. Other saturated nitriles: $(\text{CH}_3)\text{CH}_2\text{CN}$, $(\text{CH}_3)_2\text{CHCN}$, $(\text{CH}_3)_3\text{CCN}$

Sequential substitution of each hydrogen atom in CH_3CN with a methyl (CH_3) group generates three other organic nitriles, as shown by inspection of the first four lines of Table 1. Of these three new molecules, only propionitrile

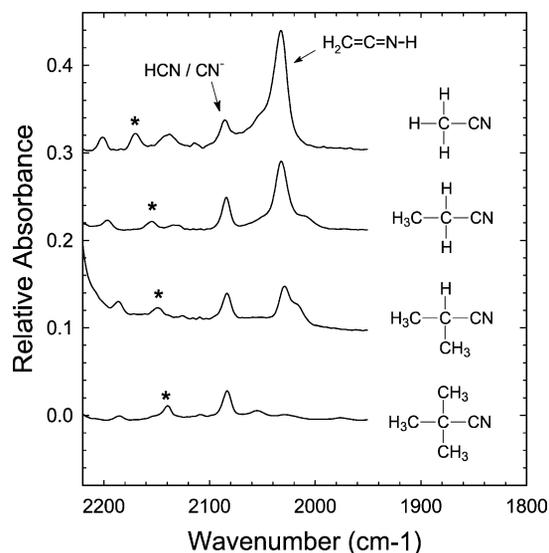


Fig. 8. Spectra of four nitriles, each shown after a ~ 90 -min UV photolysis at 12 K. The small features between 2185 and 2200 cm^{-1} were initially present in each case. Asterisks indicate isonitrile products (see text).

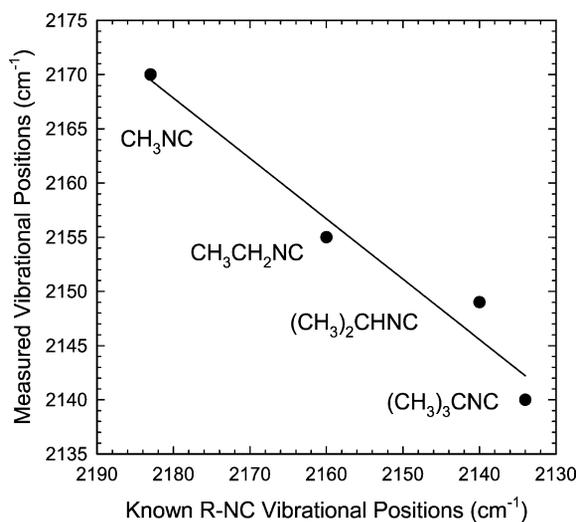


Fig. 9. Correlation of the positions marked with asterisks in Fig. 8 with liquid-phase R-NC vibrational positions (Nyquist, 2001). The uncertainties of our measured positions are about $\pm 2 \text{ cm}^{-1}$.

($\text{CH}_3\text{CH}_2\text{CN}$) is known to be interstellar; none of the three have yet been detected in a Solar System object. We investigated each of these nitriles as an indirect way to identify products from CH_3CN .

Figure 8 compares IR spectra from UV photolysis experiments on CH_3CN , $(\text{CH}_3)\text{CH}_2\text{CN}$, $(\text{CH}_3)_2\text{CHCN}$, and $(\text{CH}_3)_3\text{CCN}$. A band at $\sim 2086 \text{ cm}^{-1}$ is seen in each case, implying a common carrier. This feature is almost certainly due to HCN (Moore and Hudson, 2003), although a contribution from CN^- cannot be excluded. Supporting this assignment is the fact that HCN is a known product of both the radiolysis (Asycough et al., 1968) and photolysis (McElcheran et al., 1958) of CH_3CN .

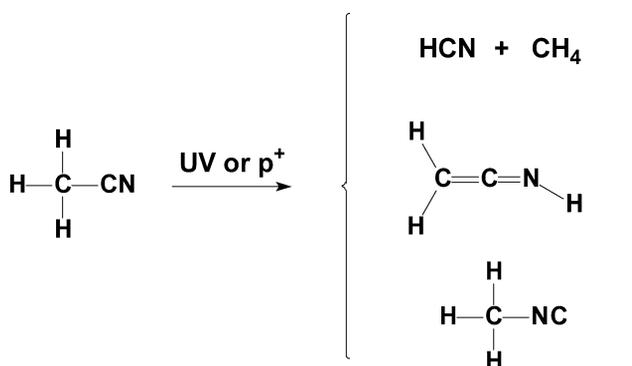


Fig. 10. Summary of reaction products discussed, from either radiolysis or photolysis of CH_3CN , in either pure CH_3CN or $\text{N}_2 + \text{CH}_3\text{CN}$.

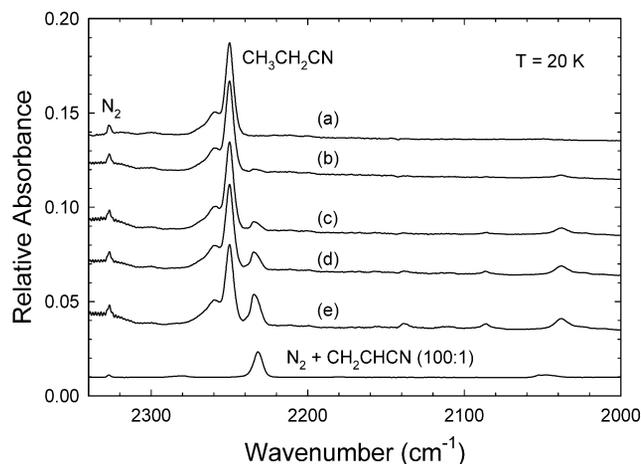


Fig. 11. IR spectra of $\text{N}_2 + \text{CH}_3\text{CH}_2\text{CN}$ (100 : 1) before (a) and after photolyses of (b) 5, (c) 15, (d) 30, and (e) 60 min. The bottom trace is a reference spectrum of $\text{N}_2 + \text{CH}_2\text{CHCN}$ (100 : 1).

For each nitrile in Fig. 8, the position marked with an asterisk is plotted in Fig. 9 against the corresponding isonitrile's $-\text{N}\equiv\text{C}$ stretching position in the liquid phase (Nyquist, 2001). The good correlation led us to assign the peaks with asterisks in Fig. 8 to isonitrile molecules. Since $(\text{CH}_3)_3\text{CNC}$ was commercially available, we were able to confirm its assignment directly by measuring its IR spectrum.

At the top of Fig. 8, the ketenimine feature is prominent at 2033 cm^{-1} . However, the corresponding band appears increasingly weak on going down the figure and through the sequence from CH_3CN to $(\text{CH}_3)\text{CH}_2\text{CN}$ to $(\text{CH}_3)_2\text{CHCN}$ to $(\text{CH}_3)_3\text{CCN}$. This is as expected since the availability of nearby H atoms for “migration” to the terminal nitrogen is decreasing.

Summarizing to this point, our experiments reveal several reaction products for simple organic nitriles. For CH_3CN these are represented in Fig. 10. The other nitriles of this section also underwent rearrangements to produce an isonitrile and, in all but one case, a ketenimine.

As for reactions not seen in CH_3CN but observed in the more complex nitriles, loss of hydrogen was found

in both the radiolysis and photolysis of $\text{CH}_3\text{CH}_2\text{CN}$. **Figure 11** shows that a 60-min photolysis of $\text{N}_2 + \text{CH}_3\text{CH}_2\text{CN}$ (100 : 1) produced CH_2CHCN , as indicated by a feature at 2234 cm^{-1} (confirmatory band at 963 cm^{-1} , not shown). Similar results were obtained after proton irradiation of $\text{N}_2 + \text{CH}_3\text{CH}_2\text{CN}$ (100 : 1), and both irradiation and photolysis of pure $\text{CH}_3\text{CH}_2\text{CN}$. The conversion $\text{CH}_3\text{CH}_2\text{CN} \rightarrow \text{CH}_2\text{CHCN}$ was seen in all four experiments.

3.3. Unsaturated nitriles (CH_2CHCN , HCCCN) and cyanogen (NCCN)

Acrylonitrile (CH_2CHCN , also called vinyl cyanide) is a known interstellar molecule. Reactions it might conceivably undergo include isomerizations to form an isocyanide or a ketenimine, eliminations of HCN or H_2 , and conversion to HCCCN . While all of these were considered in our work, our emphasis was on establishing reactions that acrylonitrile has in common with other nitriles.

Both ion irradiation and UV photolysis of $\text{N}_2 + \text{CH}_2\text{CHCN}$ (100 : 1) samples gave 2267 and 2067 cm^{-1} features characteristic of cyanoacetylene, HCCCN , the reaction being $\text{CH}_2\text{CHCN} \rightarrow \text{HCCCN}$. **Figure 12** shows the results of one experiment. A broad band at 2132 cm^{-1} can be assigned to the isonitrile, CH_2CHNC , on the basis of earlier work (**Matteson and Bailey, 1968**). No clear evidence of ketenimine formation was recorded, but a feature near 2091 cm^{-1} indicated that HCN was made. For the most part, these results agree with the earlier work of **Machara and Ault (1988)**, who used somewhat different experimental conditions to study the solid-phase photochemistry of acrylonitrile. Although we did not proton irradiate pure acrylonitrile, for fear of converting the sample into a very refractory polymer, UV photolysis of pure CH_2CHCN did produce the isonitrile and cyanoacetylene, just as in the N_2 -matrix experiments.

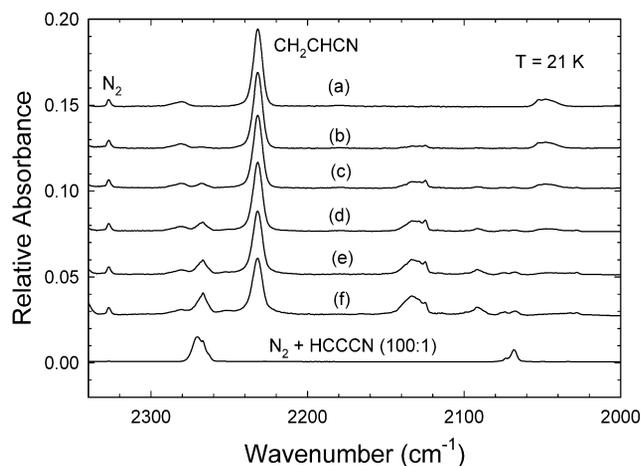


Fig. 12. IR spectra of $\text{N}_2 + \text{CH}_2\text{CHCN}$ (100 : 1) before (a) and after photolyses of (b) 5, (c) 15, (d) 30, (e) 60, and (f) 120 min. The bottom trace is a reference spectrum of $\text{N}_2 + \text{HCCCN}$ (100 : 1).

Cyanoacetylene ($\text{HC}\equiv\text{C}-\text{C}\equiv\text{N}$) has been reported in comets, in Titan's atmosphere, and in the interstellar medium, so insight into its chemistry could have broad applications. After either irradiation or photolysis of $\text{N}_2 + \text{HCCCN}$ (100 : 1) at $\sim 18\text{ K}$, the strongest feature of isocyanacetylene ($\text{HC}\equiv\text{C}-\text{N}\equiv\text{C}$) was found at 2032 cm^{-1} (**Kołos and Waluk, 1997**), but little else could be identified. Both irradiation and photolysis produced a weak band in pure HCCCN at 2200 cm^{-1} . This might be from CCCNH (**Kołos and Sobolewski, 2001**), but much more work is needed to secure this identification.

Cyanogen ($\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$) has been observed in Titan's atmosphere, but has not yet been detected in comets or the interstellar medium. Although cyanogen is not an organic nitrile, unlike other molecules considered here, we studied it both to check our understanding of nitrile chemistry and to seek possible reaction products that might be sought on Titan and elsewhere. As we expected, solid cyanogen, in common with the other $-\text{CN}$ molecules in this paper, easily isomerized to form an isonitrile: $\text{NCCN} \rightarrow \text{NCNC}$. Characteristic, pronounced IR features of NCNC were seen at 2300 and 2063 cm^{-1} (**Stroh et al., 1989**) after either UV photolysis or proton-irradiation of $\text{N}_2 + \text{NCCN}$ (50 : 1) mixtures at 12 K . No experiments on pure cyanogen were undertaken, again for fear of producing very refractory polymeric material.

3.4. Nitriles in H_2O

Since H_2O is the most abundant molecule in cometary comae and interstellar ices, we also have examined the chemistry of nitriles embedded in H_2O . Our experiments focused on radiation chemistry, as radiation experiments could be conducted with thicker samples than in photolysis experiments, due to the greater penetration of our proton beam compared to the UV photons. Thicker samples resulted in more intense product bands in IR spectra.

Figure 13 shows that proton irradiation of $\text{H}_2\text{O} + \text{CH}_3\text{CN}$ and of $\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CN}$ again gave a ketenimine feature near 2033 cm^{-1} and HCN near 2090 cm^{-1} . However, instead of the expected bands of CH_3NC and $\text{CH}_3\text{CH}_2\text{NC}$, a broad absorbance near 2165 cm^{-1} was seen. In an earlier paper (**Hudson et al., 2001**) we assigned this band to the cyanate ion, OCN^- , reporting it in irradiated $\text{H}_2\text{O} + \text{HCN}$. Its presence in the experiments of **Fig. 13** is consistent with our earlier work. Warming irradiated $\text{H}_2\text{O} + \text{nitrile}$ ices showed that ketenimine, CH_4 , and HCN were still trapped at 125 K , with some being retained as high as 150 K . The cyanate ion was easily seen as high as 200 K . In the case of $\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CN}$, a weak feature at 2234 cm^{-1} in the bottom spectrum of **Fig. 13** was suggestive of the product CH_2CHCN .

The radiation-induced decay of CH_3CN in $\text{H}_2\text{O} + \text{CH}_3\text{CN}$ (10 : 1) was followed in one experiment, and is summarized in **Fig. 14**. The initial rate of decay is similar to that in pure CH_3CN (**Fig. 5**), but a nonzero equilibrium abundance is reached. The reason for this has not been established. See

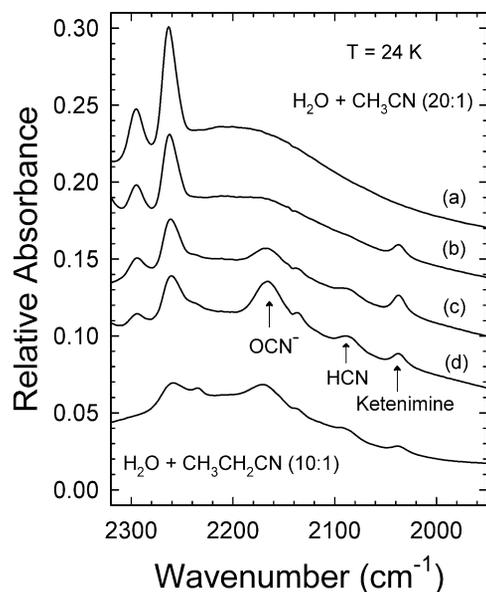


Fig. 13. IR spectra of $\text{H}_2\text{O} + \text{CH}_3\text{CN}$ (20 : 1) before (a) and after proton irradiation to about (b) 1, (c) 5, and (d) 10 eV molecule^{-1} . The bottom trace is the spectrum of $\text{H}_2\text{O} + \text{CH}_2\text{CH}_2\text{CN}$ (10 : 1) after irradiation to $\sim 5 \text{ eV molecule}^{-1}$.

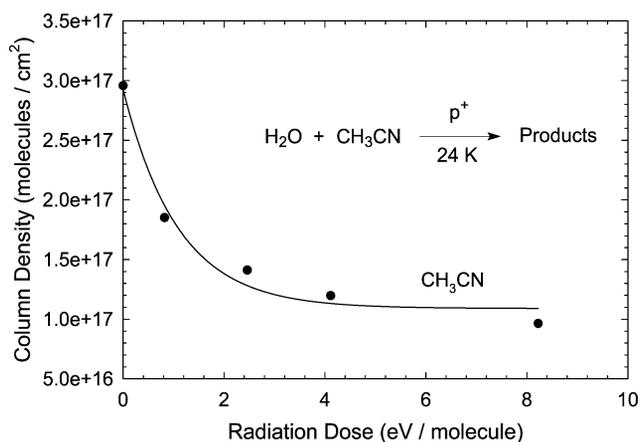


Fig. 14. Destruction of CH_3CN in $\text{H}_2\text{O} + \text{CH}_3\text{CN}$ (10 : 1) mixture at 24 K by 0.8 MeV p^+ .

Bernstein et al. (2004) for a similar observation with photolyzed CH_3CN .

Only two other organic nitriles were proton irradiated in H_2O , acrylonitrile and cyanoacetylene. Irradiation of $\text{H}_2\text{O} + \text{CH}_2\text{CHCN}$ (10 : 1) gave HCN and a clean OCN^- band, but no unequivocal evidence of an isonitrile (expected near 2133 cm^{-1}), and only a hint of HCCCN bands. However, new features at 2260, 1462, and 1384 cm^{-1} matched those of the reduction product $\text{CH}_3\text{CH}_2\text{CN}$. For cyanoacetylene, irradiation of $\text{H}_2\text{O} + \text{HCCCN}$ (10 : 1) to a dose of $\sim 2 \text{ eV molecule}^{-1}$ gave a weak OCN^- band and a hint of CH_2CHCN .

The last nitrile we studied in H_2O was cyanogen (NCCN). Again we were concerned about producing highly refractory material, so a $\text{H}_2\text{O} + \text{NCCN}$ (5 : 1) sample was only

photolyzed, not proton irradiated. The final spectrum after photolysis showed the HCN/CN^- feature at 2090 cm^{-1} and the broad OCN^- band at $\sim 2165 \text{ cm}^{-1}$. There was no evidence of isocyanogen, NCNC, even though its IR bands were well-removed from the OCN^- feature.

3.5. Residual materials

After warming to room temperature, a colored residue was sometimes left behind by samples that had been either irradiated or photolyzed, particularly in the cases of acrylonitrile, cyanoacetylene, and cyanogen. For example, irradiations of HCCCN, $\text{H}_2\text{O} + \text{HCCCN}$, and $\text{N}_2 + \text{HCCCN}$ gave black, brown, and faint yellow residues, respectively. No systematic attempt was made to characterize this residual material, IR spectroscopy being a rather insensitive analytical technique, and the samples being under a micron in thickness (surface area $\approx 5 \text{ cm}^2$). However, in two cases IR spectroscopy provided a clue to the nature of a residue. On prolonged irradiation at $\sim 18 \text{ K}$, both CH_3CN and $\text{CH}_3\text{CH}_2\text{CN}$ showed a pronounced IR feature with the shape and position ($\sim 1654 \text{ cm}^{-1}$) expected for an amine. Amine formation is intriguing as it has been reported in few earlier papers (e.g., Fujii and Arai, 1999), and could lead to acid–base chemistry. Obviously much more work is needed to characterize this, and the other, residual materials from our experiments.

4. Discussion

4.1. Reaction products

Tables 3, 4, 5, and 6 summarize IR band positions of the nitriles we studied, along with the isonitriles, ketenimines, and cyanate products observed. Previously we have seen that in most cases (Hudson and Moore, 2000, 2001, 2002), the same identifiable products are formed in chemistry induced by 0.8 MeV protons and far-UV photons, and this conclusion applies to the nitriles of this paper. However, a comparison of Figs. 6 and 7 shows that differences in the relative abundances of products exist for the two types of experiments. Ketenimine dominates over CH_3NC in the radiation

Table 3
Positions (cm^{-1}) of $\text{C}\equiv\text{N}$ stretches in amorphous solids at $\sim 20 \text{ K}$

Molecule	Pure nitrile	Nitrile in N_2	Nitrile in H_2O
CH_3CN	2252	2255	2263
$(\text{CH}_3)\text{CH}_2\text{CN}$	2246	2250	2258
$(\text{CH}_3)_2\text{CHCN}$	2245	2249	2255
$(\text{CH}_3)_3\text{CCN}$	2235	2239	2241
CH_2CHCN	2229	2232	2239
HCCCN	2268	2270	2268
	2066 ^a	2068 ^a	2066 ^a
NCCN	2345, 2336	2347	2344
	2162	2160	2162

^a $\text{C}\equiv\text{C}$ stretching vibration.

Table 4
Positions (cm^{-1}) of $-\text{N}\equiv\text{C}$ stretch in amorphous solids at ~ 20 K

Isonitrile	In parent nitrile ^a	In N_2 ^b
CH_3NC	2170	2168
$(\text{CH}_3)\text{CH}_2\text{NC}$	2155	2149
$(\text{CH}_3)_2\text{CHNC}$	2149	2147
$(\text{CH}_3)_3\text{CNC}$	2140	2141
CH_2CHNC	~ 2132	~ 2132
HCCNC	^c	2032
NCNC	^d	2300, 2063

^a Isonitrile made by UV photolysis of the parent nitrile.

^b Isonitrile made by UV photolysis of N_2 + parent nitrile (100 : 1).

^c IR band too weak to reliably measure position.

^d Experiment not done.

Table 5
Positions (cm^{-1}) of ketenimine bands in amorphous solids at ~ 20 K

Parent nitrile	Ketenimine formed	In parent nitrile ^a	In N_2 ^a	In H_2O ^b
CH_3CN	$\text{H}_2\text{C}=\text{C}=\text{NH}$	2033	2038	2037
$(\text{CH}_3)\text{CH}_2\text{CN}$	$(\text{CH}_3)\text{HC}=\text{C}=\text{NH}$	2032	2038	2038
$(\text{CH}_3)_2\text{CHCN}$	$(\text{CH}_3)_2\text{C}=\text{C}=\text{NH}$	2029	2029	2031

^a Ketenimine species made by UV photolysis of the parent nitrile.

^b Ketenimine species made by p^+ irradiation of the parent nitrile.

Table 6
Cyanate anion band positions (cm^{-1}) in amorphous solids at ~ 20 K

Ice sample	Position
$\text{H}_2\text{O} + \text{CH}_3\text{CN}$ (10 : 1)	2166 ^a
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CN}$ (10 : 1)	2167 ^a
$\text{H}_2 + (\text{CH}_3)_2\text{CHCN}$ (8 : 1)	2166 ^a
$\text{H}_2\text{O} + \text{CH}_2\text{CHCN}$ (20 : 1)	2168 ^a
$\text{H}_2\text{O} + \text{HCCCN}$ (10 : 1)	2163 ^a
$\text{H}_2\text{O} + \text{NCCN}$ (5 : 1)	2168 ^b

^a Cyanate anion made by p^+ irradiation of the ice sample.

^b Cyanate anion made by UV photolysis of the ice sample.

experiment, but the reverse is true in the photolysis experiment. Also, a comparison of these two figures shows that $\text{H}_2\text{C}=\text{C}=\text{NH}$ and CH_3NC go through maxima only in the radiation experiment. Careful rate and dose measurements are needed to determine if these maxima are simply due to energy dose differences, differences in p^+ and UV penetration, or whether another factor is operative. The general shapes of our CH_3NC and $\text{H}_2\text{C}=\text{C}=\text{NH}$ curves in Figs. 6 and 7 are reminiscent of work reported by (Baratta et al., 2002; Fig. 6) for the $\text{CH}_4 \rightarrow \text{C}_2\text{H}_6$ reaction. In that case, optical properties of the solid CH_4 influenced product formation.

More important for the chemistry than the energy source were the three environments we used to investigate nitrile chemistry (bulk nitriles, N_2 , and H_2O), since these did give different reactions products. In the absence of H_2O , isonitriles were detected, as summarized in Fig. 15. That we see nitrile-to-isonitrile conversions in N_2 is not surprising, as they have been observed in rare-gas matrices (e.g., Milligan and Jacox, 1967). Less expected is that these reactions also

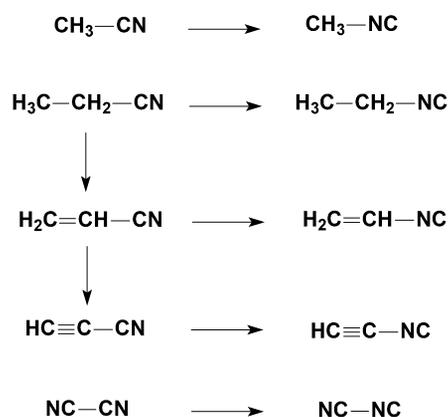


Fig. 15. Isonitriles from either radiolysis or photolysis of nitriles in the absence of H_2O . In the cases of acetonitrile and propionitrile, formation of a ketenimine was also observed.

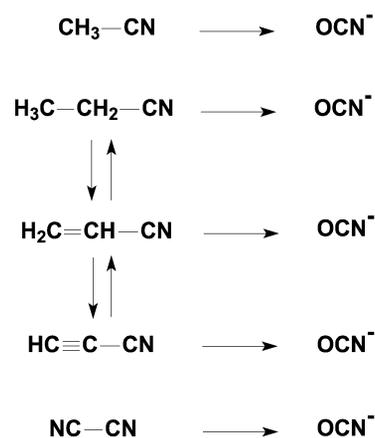


Fig. 16. Cyanates from either radiolysis or photolysis of nitriles in the presence of H_2O . In the cases of acetonitrile and propionitrile, formation of a ketenimine was also observed.

occurred in pure nitriles. Other reactions seen in the absence of H_2O were the loss of hydrogen to form “oxidized” products, indicated by the vertical, downward arrows of Fig. 15, and, for some nitriles, the formation of ketenimines already discussed.

In contrast to the isonitrile synthesis under anhydrous conditions, no ice experiment involving H_2O gave evidence for an isonitrile, but rather OCN^- was seen in each case, as indicated in Fig. 16. This figure also shows that loss of hydrogen took place (vertical, downward arrows) in some nitriles, but that hydrogen addition (vertical, upward arrows) was also seen. The mechanisms by which H loss or gain occurred are still unknown, but H_2 elimination and H-atom addition, respectively, are possibilities.

Since an anion (OCN^-) was seen in experiments with H_2O and a nitrile, the question of the corresponding cation arises. The hydronium ion (H_3O^+) is an obvious candidate, but its weak, broad bands, overlapping with those of H_2O , will make its identification very difficult (Delzeit et al., 1993). If amines were made in our experiments (Section 3.5), then the counterion to OCN^- is probably a protonated amine. Amine formation would open up possibilities

for acid–base reactions, such as converting the HCN formed in our reactions into CN^- . More work on the solid-state conversion $-\text{C}\equiv\text{N} \rightarrow \text{CH}_2\text{NH}_2$ is needed before anything definite can be said.

4.2. Astrochemical considerations

In an earlier paper (Moore et al., 2001) we estimated the cosmic-ray and UV doses available to both interstellar and cometary ices. In a dense molecular cloud, ices are estimated to receive both particle and photon doses on the order of a few eV molecule⁻¹ during the clouds's lifetime. Such doses are the same order of magnitude as in our experiments (e.g., Fig. 5), so a similar nitrile chemistry is expected. In contrast, diffuse interstellar clouds are thought to receive millions of eV molecule⁻¹ from UV photons over their lives, so that the chemistry we report here could only be seen over a small time period. Cometary ices, after accretion, experience doses that fall with distance from a comet's surface. Our doses of a few eV molecule⁻¹ are thought typical of cometary ice at a depth of a few meters, integrated over the age of the Solar System.

Nitriles formed in the atmosphere of Titan are expected to precipitate down onto the satellite's surface (Flasar, 1998; Lara et al., 1996) where cosmic radiation can convert them into other molecules. Sagan and Thompson (1984) estimated that surface ices on Titan receive a radiation flux of about 5.6×10^7 eV cm⁻² s⁻¹. Our laboratory experiments require about 10^3 s for a radiation dose of about 10^{14} p⁺ cm⁻² to CH_3CN , for an energy flux of $\sim 2.3 \times 10^{15}$ eV cm⁻² s⁻¹. This means that the chemistry we see in the laboratory in 10^3 s would require about 10^3 years on Titan's surface. Unfortunately, little is directly known about geological activity on Titan, so that complications such as possible resurfacing and subduction of material over 10^3 years are difficult to estimate.

Our experiments show that the type of nitrile reaction products on Titan's surface will depend on whether or not H_2O ice is present. Isonitriles and ketenimines should form in "dry" surface regions, since we observed the synthesis of these molecules in both reactive organic material (pure nitriles) as well as the less reactive N_2 . These conversions of nitriles into isonitriles and ketenimines appear to be intramolecular (involving only a single molecule), which implies that these products will form in a variety of organic media. We also expect that some Titan nitriles lose H atoms (see Fig. 15), becoming more susceptible to surface polymerization.

According to our warming experiments, all photo- and radiation chemical products should remain trapped in H_2O -rich ices for temperatures of ~ 100 K, and probably much higher. However, the possibility of the reconversion of ketenimine to the more stable CH_3CN over long times should be considered. The data of Doughty et al. (1994) show that near 1500 K, gas-phase $\text{H}_2\text{C}=\text{C}=\text{NH}$ reverts to CH_3CN with a half-life of about 0.001 s. Extrapolation of the Doughty et

al. (1994) results to 100 K gives a ketenimine half-life of about 10^{124} years. Although extrapolations over such a wide temperature range can be very unreliable, we feel confident that for most astrochemical environments, ketenimine will be stable at $T < \sim 100$ K with respect to isomerization to acetonitrile. Similar comments apply to the stability of the CH_3NC product, with respect to CH_3CN (Schneider and Rabbinovitch, 1962).

Titan's surface is usually considered to be dominated by liquid organics (Campbell et al., 2003), but recent work of Griffith et al. (2003) suggests that regions of H_2O -ice may be exposed. Our experiments show that radiation would still produce ketenimine from CH_3CN if frozen H_2O is present, and that this compound would remain trapped in the ice. The cyanate ion (OCN^-) would also be a stable radiation product in any Titan region having both nitriles and H_2O -ice.

Conclusions similar to the above apply to nitriles in irradiated or photolyzed cometary ices. Two organic nitriles have been identified in comets, CH_3CN and HCCCN , but no organic isonitriles have yet been found. In cometary ices there can scarcely be any doubt that frozen H_2O is present, and our experiments demonstrate that the $\text{XCN} \rightarrow \text{XNC}$ conversion is not seen in H_2O -ice. Irradiation or photolysis of cometary ices will produce OCN^- from nitriles. In the case of cometary HCN, the corresponding isonitrile (HNC) has been observed, and is of much interest. However, experiments on both irradiated (Hudson et al., 2001) and photolyzed (Gerakines et al., 2004) $\text{H}_2\text{O} + \text{HCN}$ ices show evidence for OCN^- formation, but not for HNC synthesis. It does not appear likely that the work reported here controls the cometary HNC-to-HCN ratio (Rodgers and Charnley, 2001). Our experiments do imply that ketenimine formation in cometary ice is likely, as are syntheses of CH_2CHCN and $\text{CH}_3\text{CH}_2\text{CN}$, perhaps by low-temperature H-atom addition to HCCCN .

Interstellar ices are dominated by H_2O , and neither HCN nor any organic nitrile has been identified in them. However, these same solids show an intense IR feature due to OCN^- (Hudson et al., 2001), as expected if nitriles are trapped in interstellar ices and then irradiated or photolyzed. Our experiments can be seen as another demonstration of the ease with which OCN^- is formed.

The gas-phase molecules of the interstellar medium (ISM) provide many intriguing examples of nitrile chemistry, including the following:

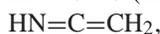
- nitrile/isonitrile pairs: HCN/HNC , $\text{CH}_3\text{CN}/\text{CH}_3\text{NC}$, $\text{HCCCN}/\text{HCCNC}$;
- organic nitriles: CH_2CHCN , $\text{CH}_3\text{CH}_2\text{CN}$, H_3CCCCN ;
- the HC_nCN ($n = 0, 2, 4, \dots, 10$) series;
- inorganic nitriles: MgCN , NaCN , and NH_2CN ;
- inorganic isonitriles: MgNC and AlNC ;
- ions and unstable species: HNCCC , CN , HCCN , HCNH^+ , HC_3NH^+ , CH_2CN .

The interstellar presence of the CH₃CN/CH₃NC and HC₃CN/HCCNC pairs we studied suggests that other organic isonitriles may await detection, such as CH₂CHNC and CH₃CH₂NC.

As for ketenimines, interstellar H₂C=C=NH was discussed by Green and Herbst (1979) over 25 years ago, but it has yet to be identified in the ISM. Nevertheless, the readiness with which this molecule formed in our experiments suggests that it could be synthesized in interstellar space, either on grain surfaces or in ice mantles on grains. Furthermore, we note that this molecule's "X=Y=Z" framework is identical to that of several known interstellar molecules. For example, ketene and ketenimine



and also isocyanic acid and ketenimine (written in reverse)



are isoelectronic pairs with a common geometry. The suggestion here is that this "X=Y=Z" molecular framework may be quite common in the ISM. Other, perhaps less obvious, interstellar examples include O=C=O, N=N=O, and the ion O=C=N⁻. (Some as-yet-undetected examples include H₂C=C=CH₂, H₂C=N=N, HN=N=N, and N=N=N⁻.)

Assuming that solid-phase reactions yield the chemical species outlined in this paper, what are the prospects for detections? For Titan, comets, and the ISM, microwave and mid-IR spectra appear to hold the best prospects for the immediate future. The interstellar isonitriles have known rotational spectra, and these can be used for observational searches on Titan and in cometary comae. Similarly, microwave (Rodler et al., 1984) and mid-IR (Ito et al., 1990) data are available for gas-phase H₂C=C=NH. Infrared spectra at reasonably high resolution also have been published for OCN⁻ (Gruebele et al., 1987).

4.3. Astrobiological considerations

Our work was designed to reveal low-temperature photo- and radiation products of nitriles, but there may be connections to prebiotic chemistry. As already mentioned, some of our experiments gave a residual material about which we know little. Our irradiated/photolyzed organic nitriles may have been reduced to amines by H-atom addition to the C≡N group, in which case they would participate in acid–base chemistry. Careful chromatographic analyses are needed to check for any amines. It is also desirable to analyze residues from H₂O-ice experiments since Draganić et al. (1976) found amino acid formation in irradiated solutions of CH₃CN and CH₃CH₂CN. Finally, Sanchez et al. (1966) reported that aqueous solutions of OCN⁻ and HCCCN produced cytosine, a component of DNA. Since the OCN⁻ ion was made in our experiments with H₂O + HCCCN, the formation of cytosine would not be unreasonable in this mixture. Amino acids or cytosine made at low temperatures, by

either cosmic-ray bombardment or far-UV photons, would be available for injection into the gas phase or, in the case of comets, delivery to the early Earth.

5. Conclusions

Some of our more important conclusions are summarized below.

- (1) Both UV-photolysis and p⁺ bombardment of either CH₃CN or N₂ + CH₃CN ices produce the isomer H₂C=C=NH. This product is also seen after either UV-photolysis or p⁺ bombardment of H₂O + CH₃CN mixtures. Similar results were found for CH₃CH₂CN and (CH₃)₂CHCN.
- (2) Isonitriles are detected after either UV-photolysis or p⁺ bombardment of the nitriles examined, but not in H₂O-rich ices.
- (3) In H₂O-rich ices, the nitriles studied produced OCN⁻, with no evidence of isonitrile formation.
- (4) Formation of HCN was seen in all experiments.
- (5) The observed products in either pure nitriles or H₂O mixtures are trapped in the solid ice until ~ 100 K, and in some cases much higher temperatures.

Acknowledgments

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